Module IV, ELECTROCHEMISTRY & CORROSION

ELECTROCHEMISTRY is the branch of chemistry which deals with the study of inter-conversion of electrical energy and chemical energy.

Oxidation may be defined as a process in which an atom or an ion loses one or more electrons. Eg.

$Na \longrightarrow Na^+ + e^-$ $\qquad$ $Mg \longrightarrow Mg^{2+} + 2e^-$

Reduction may be defined as a process in which an atom or an ion gains one or more electrons. Eg.

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $\qquad$ $Cl_2 + 2e^- \longrightarrow 2Cl^-$

A chemical reaction in which both oxidation and reduction occur simultaneously is called **redox reaction. Eg**

$$\mathbf{2Mg + O_2 \longrightarrow 2MgO}$$

(Oxidation $Mg \longrightarrow Mg^{2+} + 2e^-$ & Reduction $O + 2e^- \longrightarrow O^{2-}$)

In MgO magnesium exists as Mg^{2+} and oxygen exists as O^{2-}

Conductors - Substance which allow the passage of electric current through them are called conductors. Eg. Metals, graphite, ionic compounds in fused state or in dissolved state.

Insulators - Substance which does not allow the passage of electric current through them are called insulators. Eg. glass, wood, paper etc.

Semiconductors– The conductivity of semiconductors are intermediate between conductors and insulators. Eg Silicon, Germanium etc.

Conductors have been broadly classified into **Metallic conductors & Electrolytic conductors** (Electrolytes)

Metallic conduction	Electrolytic Conduction
Conductance is due to the movement of free electrons	Conductance is due to movement of ions
No chemical change take place	Chemical change (Electrolysis) take place
There is no transfer of matter	There is transfer of matter in the form of ions
Conductance decreases with increase of temperature	Conductance increases with increase of temperature
Eg. Metals and their alloys	Eg. Ionic compounds in molten state or dissolved state

Electrolytes - Electrolytes are the substances which conduct current in the molten state or in the aqueous solution state. Eg. NaCl, KOH, HCl etc

Non electrolytes are the substances which do not conduct electricity in the fused state or in the aqueous state. Eg sugar, urea, alcohol etc

Strong Electrolytes - Electrolytes that dissociates almost completely in to ions even at moderate concentration are called strong electrolytes. Eg. strong acids and bases (HCl, NaOH etc)

Weak electrolytes- Electrolytes which dissociates into ions partially at moderate concentrations are called weak electrolytes. Eg. weak acids and bases (Acetic acid, Sodium carbonate etc)

Electrolysis is the process of decomposition of an electrolyte by the passage of electricity through it. The apparatus used for electrolysis is called **electrolytic cell**.

Faraday's First law of electrolysis – The first law states that the mass of a substance deposited or liberated at an electrode is proportional to the quantity of electricity passed. Mathematically it can be written as

W α Q , or, W = Z Q , where W is the mass of substance, Q is the quantity of current in coulomb and Z is the electrochemical equivalent of the substance. (**Q = I x t , one ampere current flowing for one second)**

W = ZQ When Q =1, then W = Z

So, ***Electrochemical equivalent Z of a substance is defined as the mass of the substance deposited or liberated by the passage of one coulomb of electricity through the electrolytes.***

(On Faraday of charge is 96500 Coulomb. It is the charge carried by 1 mole of electrons)

Faraday's Second law of electrolysis – The second law states that when same quantity of current is passed through different electrolytes, the mass of mass of substance deposited is directly proportional their chemical equivalents. Mathematically it can be written as , **W1 α E1 , and W2 α E2** , where W1 and W2 are the mass of substance 1 and substance 2, E1 and E2 are the equivalent weights of substance 1 and substance 2).

Or, $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

Applications of electrolysis – 1. Electroplating, 2. Electrolytic refining of metals 3. Anodizing, 4. Production of metals, 5. Production of non metals, 6. Production of compounds like NaOH, KOH etc.

Electroplating - The process of coating a superior (Noble) metal on an inferior metal (base metal) by passing electric current is called electroplating.

The base metal object which is to be coated is made the cathode and a pure rod of noble metal is made the anode. The electrolyte is a solution of soluble salt of the noble metal. On passing direct current the anode metal dissolve in the electrolyte and get deposited on the base metal object.

Electroplating of mild steel spoon with Nickel – In the electrolytic cell nickel plate is taken as the anode and the steel spoon is placed as the cathode. Electrolyte is the solution of nickel sulphate. When current is passed, the anode nickel dissolved in the solution and got deposited over the steel spoon.

Anode Reaction - **$Ni \rightarrow Ni^{2+} + 2e^-$ (Oxidation)**

Cathode Reaction - **$Ni^{2+} + 2e^- \rightarrow Ni$ (Reduction)**

Electrolytic refining of metal is the process of purifying a metal by electrolysis.

Electrolytic refining of copper – Impure copper is taken as anode and a pure strip of copper is taken as cathode. Copper sulphate is used as the electrolyte. When current is passed through the electrolytic cell impure copper

dissolves in the electrolyte as copper ions (Cu^{2+}) and moves towards the cathode. At the cathode copper ions deposited as copper atom.

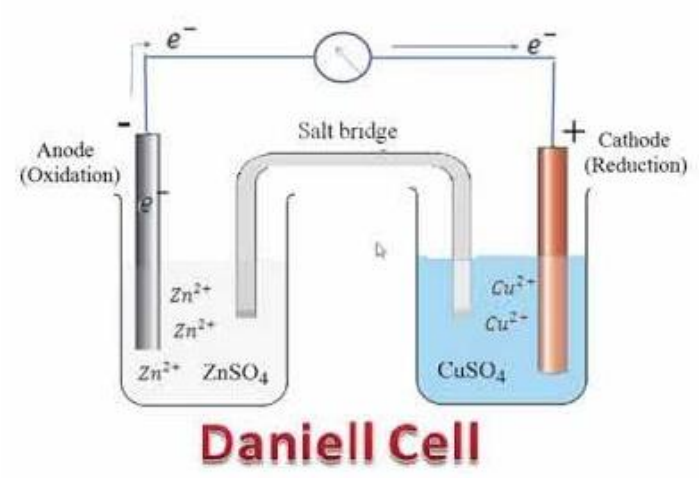
Anode Reaction - $Cu \rightarrow Cu^{2+} + 2e^-$ **(Oxidation)**

Cathode Reaction - $Cu^{2+} + 2e^- \rightarrow Cu$ **(Reduction)**

The net result is the transfer of copper atoms from impure anode to the pure copper cathode.

Electrochemical Cell (Galvanic Cell or Voltaic cell) - The device in which chemical energy is converted into electrical energy is called Galvanic cell. Eg Daniel Cell

Daniel cell consists of Zinc rod dipped in zinc sulphate solution and copper rod dipped in copper sulphate solution. The two solutions (two half cells) are connected externally by a metallic wire to a galvanometer and internally by a salt bridge. (It is an inverted U shaped glass tube filled with a jelly and an electrolyte)



Electrode reactions are,

Anode, $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Cathode, $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

Overall reaction

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

The functions of salt bridge are-

- It completes the electrical circuit internally
- It maintains the electrical neutrality of the two solutions
- It prevents the intermixing of the two solutions.

Distinction between Galvanic cell and Electrolytic cell

Galvanic cell	Electrolytic cell
Chemical energy is converted to electrical energy	Electrical energy is converted into chemical energy
Electrical energy is produced by a redox reaction.	Electrical energy is required for the redox reaction
Anode is negative and Cathode is positive	Anode is positive and cathode is negative
Salt bridge is generally used	No salt bridge is required

Galvanic cells are classified into – 1. Primary cells & 2. Secondary cells.

Primary cells – These are the cells in which the redox reaction occurs only once. The chemical reaction in these cells is not reversible. Eg Daniel cell, Dry cell, Mercury cell etc.

Secondary Cell – These are the cells in which the chemical reaction taking place can be reversed by passing electricity. They can be used again and again. Eg Nickel Cadmium Cell, Lead storage battery etc.
Fuel cells – Fuel cells are galvanic cells in which chemical energy of combustion of fuel is converted to electrical energy. Eg. Hydrogen – Oxygen fuel cell

Standard electrode potential –The potential of an electrode at 25^o C and one molar concentration of its ions is called standard electrode potential.
Electromotive Force (emf) – A galvanic cell is made up of two half cells namely oxidation half cell (anode) and reduction half cell (cathode). The difference in potential of two half cells (cathode and anode) of a cell is known as emf of cell.

or EMF = $E_{cathode}$ - E_{anode}

Eg. EMF of Daniel cell = E_{Cu} - E_{zn} = + 0.34 - (- 0.76) = <u>1.1V</u>

Electrochemical series - Electrochemical series is an arrangement of elements or electrodes in the increasing order of their standard reduction potentials.

Corrosion – It is the process of decay of metals due to the attack of atmospheric gases on the surface of the metal. Eg Rusting of iron.

Factors affecting corrosion - 1. Purity of metal, 2. Presence of air and moisture, 3. Presence of electrolytes, 4. Temperature (Corrosion generally increase with rise in temperature), 5. Presence of acidic gases, 6. pH of the medium, 7. Oxidation potential of the metal.

Prevention of Corrosion (or Rusting) - The important methods to prevent (or to minimize) corrosion are
1. Barrier protection – In this method, suitable coating film is placed between the metal and the surrounding air. The coating may be metallic, non-metallic and organic in nature.

(a) Metallic coating – The metal can be protected by coating with a less active metal or by coating with a more active metal. Coating of Tin over iron article is an example of protecting a metal by coating with less active metal.
Coating iron articles with Zinc is the example of protecting a metal by coating with more active metal. The more active zinc is acting as anode and undergo decay while the iron article is protected. Coating of iron articles with zinc metal is called **Galvanization**. The method of protecting a metal article by covering with a more active metal is called **Sacrificial Protection**

(b) Non-metallic coating – This include protecting a metal by coating with phosphate, chromate or Oxide film. Oxide film is generally applied by Anodizing.

(c) Organic coating –Plastic, Rubber etc can be coated over metal articles to protect from corrosion.

2. Electrical Protection (Cathodic Protection) - In this method the metal article is connected to a more active metal like Magnesium through a wire. The more active metal acts as anode and damaged, while the less active metal article is protected.

3. Antirust solution – Alkaline solutions of phosphate or chromate is applied over the metal articles to prevent corrosion. The alkaline solution removes the H^+ ions from the medium and hence corrosion is not occurred.